

QUANTITATION OF BURIED CONTAMINATION
BY USE OF SOLVENTS

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INTRODUCTION

This report for January through June 1974 describes experiments directed at determining the potential of reclaimed silicone polymers for reuse. The discovery that amines can dissolve cured silicone resins^{1, 4} has been recognized as potentially providing two "spinoffs". These are (1) recovery of silicone resins from used silicone furniture molds and (2) silicone coating of heat sensitive materials. Both of these processes could be of some importance to the national interest. The former involves recycling of products prepared from raw materials that are in short supply. The latter may lead to new coating technology that would broaden the scope of silicone use. Silicone polymers are, to a large extent, derived from sources other than petroleum (currently the methyl and phenyl side groups are incorporated from petroleum derived raw materials, however); thus, increased use of silicones would ameliorate petroleum raw material shortages, and in the long run may provide an alternative raw material to the petrochemicals used currently in nearly all other coatings.

The Inventions and Contributions Board of NASA has been informed of the discovery described above, and attempts to prepare a patent application have been reported. A request for waiver of NASA patent rights is currently being held in abeyance pending determination of our intent to submit a patent application. North Dakota State University has one of the typical patent application agreements frequently negotiated between universities and Research Corporation, 405 Lexington Avenue, N. Y. City, N. Y. 10017. At our request, Research Corporation reviewed a report⁵ submitted for consideration of a patent application and, after a long delay, reported that they would not submit an application because (a) the solvents used in the reclaiming process were so common that

it would be difficult to prove a violation should one occur and (b) the specifics of reuse of the reclaimed material had not been adequately worked out. Subsequently to this decision, we obtained permission from the Inventions and Contributions Board to allow private companies the opportunity of considering product development research related to (b) above. At present, a large paint company is considering the feasibility of development of processes using the amine solubilization technology. If the technology is used commercially, a delay in disclosure or a sharing of patent rights will be negotiated.

RESULTS AND DISCUSSION

Reuse of reclaimed silicone polymer solutions would be greatly facilitated if crosslinks were regenerated during solvent evaporation. Based on the mechanism as presented previously,^{1, 3} it was anticipated that a significant number of crosslinks would reform on evaporation of the amine solvent. One approximate measure of the extent of crosslinking is the weight fraction that cannot be extracted; the greater the nonextractable fraction, the greater the number of crosslinks. The extraction in this case was carried out in refluxing acetone for 48 hours using a Soxhlet extractor. Free films of both the original and reclaimed polymer were weighed before and after extraction with the results presented in Table I. If the amine solvent was not removed, the whole sample was essentially extractable. Thus, the results presented for the reclaimed samples indicate that crosslinks are reformed and that conditions during solvent removal affect the extent of recrosslinking. Contrary to the trend suggested in Table I, the extent of recrosslinking did not continue to increase indefinitely as the temperature of drying increased as indicated by lower levels of % nonextractable when films were dried at 230°C. It is difficult to predict optimum

recrosslinking conditions because the reaction may depend on a complex set of reaction rate constants and evaporation rates. It is felt that the DC840 silicone considered in Table I is typical of oven cure resins of the poly(methylphenylsiloxane) type. The structure of DC840 has been studied thoroughly⁸.

Silicone rubber as well as cured silicone resins were subjected to tests of recovery of properties after evaporation of solvent following dissolution in amines. Results of tensile property determinations for a silicone rubber consisting of lightly crosslinked poly(methylsiloxane) are given in Table II. It is clear that some of the "rubbery" properties are recovered indicating that crosslinks are reformed. However, extended storage periods in the dissolved state clearly alter the structure as indicated by reductions in both tensile strength and percent elongation. Tensile properties were determined on an Instron instrument using widely accepted procedures that are described in detail elsewhere⁸.

A number of tests that are common in the coatings industry (but little known elsewhere) were carried out on dried films of DC840 and on reclaimed samples of DC840. Reclaimed samples were cast as films from a number of different amines and air dried for ten days. The control film samples were baked at 240°C for one hour; such samples dissolved in the desired amine were designated as the reclaimed material. With regard to solvent and chemical resistance tests, reclaimed samples were equal to the controls with the exception of samples dissolved in 1,2-diaminopropane. This diamine may have persisted in the air dried films due to its lower volatility. Reclaimed samples were also equal to controls in tests designed to measure hardness, again with the exception of films cast from 1,2-diaminopropane. As expected for a highly crosslinked silicone, flexibility was poor for both controls and reclaimed samples.

Although tests cannot be considered conclusive, it is encouraging to note that reclaimed films have properties that approach acceptable levels for commercial coatings. Further study appears to be worthwhile, and since product development research is not an objective of this project or of NDSU, private industry has been apprised of the possibilities. The high curing temperatures and long cure periods required for silicones have created problems with silicone coatings for a long period. The possibility of forming silicone coatings by solvent evaporation is, therefore, an attractive alternative.

PLANS FOR ADDITIONAL WORK

During the next six month period, efforts will be directed at:

- 1) Determination of the toxicity of epoxy prepolymers to spores. (Some initial results suggest a significant level of sporicidal activity.)
- 2) Investigation of sporicidal effects of high temperatures reached during epoxy cure due to exothermic chemical reactions.
- 3) Completion and submission of publications.
- 4) Use of silicone compounds in uv curable coatings that contain epoxy resins.
- 5) Assessment of patent possibilities with an input from private industry concerning product development research.

PERSONNEL

Ronald Just, a second year graduate student in the Polymers and Coatings Department, is now receiving financial support on this project in connection with (4) above. Mr. Just received his B. S. degree in 1973 from Minot State College, Minot, North Dakota; he is a native of Mandan, North Dakota.

Joseph Helm is continuing the viability study with epoxy systems as related to (1) and (2) above. Yu-Chuan (Paul) Hsiao has completed his Ph. D. degree and moved to South Bend, Indiana to join O'Brien Corporation.

Table I. The Degree of Crosslinking of Cured and Reclaimed
DC 840 by Acetone Extraction

Sample	% Nonextractable	% Nonextractability recovered
Control sample*	86.5	(100)
Reclaimed sample **		
1) dried at room temp. for 48 hrs	66.6	77.0
2) baked at 60° C for 24 hrs	65.2	75.4
3) baked at 100° C for 2 hrs	77.3	89.4

*Cured at 240° C for 1 hour.

** Prepared by dissolving the control sample in n-butylamine and removing solvent under specified conditions.

Table II. Tensile Strength and Percent Elongation of Cured and Reclaimed Dow Corning Silastic J Silicone Rubber

Sample	Tensile strength		Elongation	
	Modulus	% recovered***	%	% recovered***
	(dynes/mm ²)			
Control sample*	5.07×10^5	100	123	100
Reclaimed sample**				
Cured Silastic J dissolved in n-butylamine for:				
5 days	2.89×10^5	57	103	83
10 days	2.49×10^5	49	88	71
60 days	1.47×10^5	29	78	63

* Prepared as recommended by manufacturer.

** Prepared by dissolving the control sample in n-butylamine, retaining in solution for the specified number of days, and then preparing the sample specimen by evaporation of amine at room temperature for 10 days.

*** % recovered = (100) reclaimed sample/control sample.

REFERENCES

1. S. P. Pappas, Y. P. Hsiao, and L. W. Hill, "Quantitation of Buried Contamination by Use of Solvents," Semiannual Progress Report, July-December, 1973, NASA Grant No. NGR35-001-012.
2. *ibid*, Semiannual Progress Report, January-June, 1973.
3. *ibid*, Semiannual Progress Report, July-December, 1972.
4. *ibid*, Semiannual Progress Report, January-June, 1972.
5. Y. P. Hsiao and L. W. Hill, "Solubilization of Cured Silicone Resins in Amine Solvents; A Report Submitted for Consideration of a Patent Application," May 1973, NASA Grant NGR35-001-012.
6. A. E. Rheineck and R. A. Heskin, "Quantitation of Buried Contamination by Use of Solvents; Solvent Degradation of Amine Cured Epoxy Resins"; First Interim Report, prepared by L. W. Hill, February 1972, NASA Grant NGR35-001-012.
7. R. A. Heskin, "Solvent Degradation and Exotherm Studies of Amine-Cured Epoxy Resins," Ph. D. Thesis, North Dakota State University (1971).
8. Y. P. Hsiao, "Solubilization and Spore Recovery from Silicone Polymers," Ph. D. Thesis, North Dakota State University, in press.